



Development of a highly sensitive sampler for atmospheric monitoring of 8-H ambient ozone concentrations

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ABSTRACT

A new passive sampler reinforced with a composite membrane was developed to determine the 8-h ozone (O₃) concentration in ambient air. The composite membrane's water absorption capacity and porosity values were found analyzing its surface morphology using Scanning Electron Microscopy (SEM). Ozone adsorption performance of this sampler was tested by a badge-type sampler and automated measurement results. The developed sampler gave results equivalent ($R^2 = 0.85$) to those of automated O₃ monitors, and its experimental sampling rate was determined to be 55 cm³/min, approximately two times higher than the rate of the badge-type sampler. The detection limit obtained (5.3 µg/m³, 8 h sampling) in the study was adequate for winter-period samplings where in the ozone concentration is low in urban and semi-urban areas. Multimedia sampling results revealed that the results of the developed passive sampler had a high repeatability (RSD < 20%). Passive samplers reinforced with composite membranes were tested by badge-type samplers performing simultaneous samplings in land conditions. Area sampling results indicated that badge-type samplers were not suitable for 8-h area samplings, but tube-type samplers could be used.

Keywords: Atmospheric monitoring, Chitosan, Ozone, Passive sampler, Polyethylene glycol

1. Introduction

The Air Quality Standard is specified as 120 µg/m³ (maximum 8-h mean value) in the European Directives for ozone to protect human health [1]. Automated analyzers or active sampling methods allowing continuous measurements and featuring an expensive ultraviolet (UV) photometry technique are used for the tropospheric ozone measurements. The measurement of ozone, which is in high concentration levels in rural areas, is difficult by these techniques. In recent years, alternative strategies have been developed to active sampling and automated analyzers [2, 3]. The use of passive samplers in high pollutant concentration areas is an alternative strategy to automated analyzers. Recently, the rate of using passive samplers has increased in studies evaluating the spatial distribution of tropospheric ozone and other pollutants [4-7]. A typical passive sampler consists of a collecting medium with a high affinity for the related pollutant and a static region between the atmosphere and the collecting medium where diffusion takes place. Gas molecules diffuse between the static regions after passing a barrier, and then are collected on samplers by sorption onto the collecting medium [8]. Passive samplers are prepared by different configurations (tube

[7, 9] and badge [10-13]) and techniques. Various sorption reagents such as DPE (1, 2-di (4-pyridyl)-ethylene) [14-16], nitrite [17, 18], indigo [19], indigo/carmine compounds [20, 21] are used on the collecting medium. However, because reagents, except for DPE and nitrite, do not specifically react with O₃, they can react with other air pollutants in the atmosphere such as mono-nitrogen oxides (NO_x) and polyacrylonitrile (PAN), resulting in positive errors [18, 22]. Two factors that affect the sampling rate of passive samplers are the face velocity and photolysis, which are related to sun light. The temperature effect on the sampling rate is less in membrane-transitive passive samplers. It was determined that the use of polyethylene (PE) membrane in passive samplers increased gas permeability and the performance of the sampler by acting as a diffusion barrier [23-25]. However, despite all those technological advances, suggested sampling time is two weeks in commercial passive samplers, and it can be said that a comparison of the values obtained from these samplers with the 8-h maximum limit value is not a realistic case. This study aims to decrease the sampling time and increase the overall performance. For these purposes, a new tube-type passive sampler was developed by employing a DPE coated silica gel as a collection medium and a porous and



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biodegradable membrane made of chitosan (CS)/polyethylene glycol (PEG) composite cross-linked by a natural sugar as a turbulence limiting diffuser. CS, featured as a diffusion barrier in the sampler, is a biodegradable, non-toxic, non-mutagen, and high porous polymer used in numerous sectors such as, paper production, textile paint, heavy metal chelation, wastewater treatment, cosmetics, biomedical applications, and drug production. PEG, on the other hand, was used to enhance the chemical resistance of the CS [26, 27]. Non-toxic or non-mutagen invert brown sugar, a biological cross-linker, was used for the preparation of the CS/PEG membrane in this study instead of a chemical cross-linker to preserve the water balance of the membrane and to increase its flexibility and tensile strength. The sampling rate of the classical passive sampler was increased by the membrane, imparting an 8-h ozone sampling period feature. In the station performing continuous ozone measurements by automated O₃ monitors, the sampling rates of the samplers were compared by performing simultaneous samplings using a badge-type passive sampler, developed in Eskişehir University at the department of Environmental Engineering, and a tube-type sampler, reinforced with a composite membrane. The repeatability of the developed sampler was determined by multimedia samplings. Moreover, real environment trials and the validation of the developed passive sampler were conducted in the ambient air of Konya and Ankara in Turkey. The properties of both the developed passive sampler and commercial passive samplers used in ozone measurement were presented in Table 1, which also shows that the developed passive sampler has the highest sampling rate among commercial passive samplers and its detection limit is lower than the Gradko sampler and higher than the Passam and Radiello sampler [28-30].

In this study, the composite membrane has absorbed the humidity in the air and increased the molecular diffusion rates of the non-humid ozone molecules. In addition, the small pore sized structure of the developed membrane allowed the fast passage of non-humid ozone molecules and leads to the delayed breakthrough of the collecting media. Chitosan used in the composite membrane is environmentally friendly biodegradable, non-toxic, non-mutagen, and high porous polymer. The resistance to environmental factors (such as resistance to tearing and rupture) was increased using a crosslinking agent and, importantly, it is biodegradable. Another purpose of using the cross-linking agent was to retain the amine groups by forming a branched structure on the membrane, thereby increasing the hydrophilicity of the membrane. Moreover, this fea-

ture was incorporated to the membrane not using toxic or mutagenic chemicals but using brown sugar, a biological cross-linker. In ozone sampling, the detection of approximately 30% lower O₃ concentrations based on NO₂ formation as a result of photochemical reactions between ozone and NO is an important problem. The membrane with a 28% water absorption capacity increased the theoretical sampling rate by about 9 times by absorbing moisture from the air and preventing the collecting medium from exposure to direct sunlight. In passive samplers, Eddy diffusion, which causes air turbulence at the sampler inlet, shortens the diffusion path length. This study has shown that the composite membrane not only has high gas permeability but also is a good turbulence barrier. In addition, in the ozone analysis with this passive sampler, non-complex UV spectrophotometric method is used that can be specifically and generally applied in all laboratories. Low detection limits (5.3 µg/m³, 8 h sampling) allow this sampler to be used in urban, semi-rural and rural area sampling.

2. Material and Methods

2.1. Preparation of the Samplers

The upper part of the body of the classical tube-type sampler prepared in laboratory conditions as shown in Fig. 1(a) was coated by a 0.5 cm fiberglass, 4 cm silica gel (pore diameter: 0.063-0.200 mm; Merck) and 0.5 cm fiberglass, successively. A stainless steel wire and SKC Teflon filter (4 µm) were used for a diffusion barrier, and 5% deactivated silica was used for an adsorbent. Before coating, the deactivated silica was washed with water and methanol and dried by nitrogen gas at a 0.4 L/min flow rate. The inactive substance was then coated with 1.5 mL DPE aqueous solution (1,2-bis(4-pyridyl)ethylene, Aldrich) [31]. The solution was prepared by adding 45.5 mL acetic acid + 4.5 mL ultra distilled water (Milli-Q) into 0.075 g of DPE (Aldrich) weighed in precision balance. After coating, the second drying step was carried out with nitrogen gas of 0.4 L/min for 15 min. The composite membrane was synthesized using 1.34 g of CS (Fluka, deacetylation, 85%), 0.66 g of PGE (Fluka, molecular weight, 20 000) with a proportion of 70/30 (w/w) and 9 g of natural sugar in 100 mL of 2% solution of acetic acid. Researchers have used various chemicals such as glutaraldehyde [32] and cellulose acetate [33] for cross-linking reactives. Glucose

Table 1. The Properties of Both the Developed Passive Sampler and Commercial Passive Samplers Used in Ozone Measurement

Sampler Type	Inlet	Trapping Reagent	Sampling Rate (mL min ⁻¹)	Limit of Detection (LOD)	Sampling Time	Analysis
Gradko (Palms tube)	-	NaNO ₂	15.5	10 (for 4 weeks exposures)	2-4 weeks	Ion Chromatography
Ogawa	-	NaNO ₂	21.8	-	2-3 weeks	Ion Chromatography
Radiello	PE membrane	DPE	24.6	2 (for 7 d Exposures)	3-7 d	Spectrophotometry
Passam	-	NaNO ₂	11.2	2 (for 14 d exposure)	1-4 weeks	Ion Chromatography
The developed sampler	Composite membrane	DPE	55	5.3 (for 8 h)	8 h-15 d	Spectrophotometry

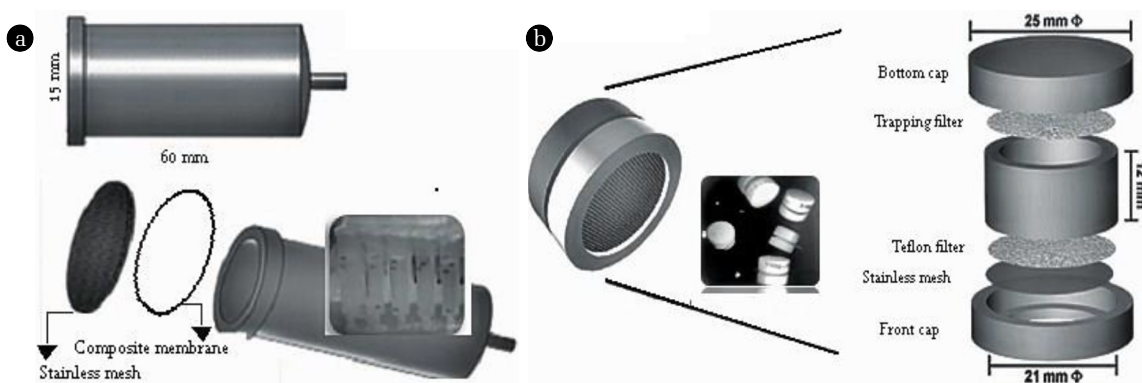


Fig. 1. Laboratory-built passive samplers (a) Tube-type, (b) Badge-type.

shows similar cross-linking properties to glutaraldehyde [34]. In this study, brown sugar (9%), a non-toxic biological cross-linker, was used as a cross-linking reactive.

After adjusting the pH value to 3-4 by HCl, Tawny-brown fluid solution was transferred to 75 mm-thick glass petri dishes in a thickness of approximately 7-8 mm and then allowed to incubate in an oven at 55°C for 8 h. After the incubation process, a circular cross-section with a 16 mm diameter was taken to determine the porosity of the membrane before the extraction treatment by hot water. The weight and volume of the membrane cross-section were measured. Afterwards, the membrane was applied to eversion in a 2% NaOH solution at room temperature (RT), and extracted in a water bath at 80°C for 8 h. Then it was dried at RT for 8 h. After the extraction process, its weight and volume were measured again. The surface morphology of the membrane was observed by 50 VP Zeiss Supra SEM equipment.

The porosity of the composite membrane was calculated using the following equation.

$$\text{Porosity (\%)} = \left(1 - \frac{\delta_1}{\delta_2}\right) \times 100 \quad (1)$$

where d_1 shows the density of the membrane cross-section after extraction, and d_2 shows the density of the membrane cross-section before extraction. It was assumed that all the pores in the membrane were completely filled with water.

The components and dimensions of the badge-type passive sampler used in the study, as shown in Fig. 1(b), are as follows: a polyethylene body, a barrier made from stainless steel wire and SKC Teflon (PTFE) filter (4 μm), a 20 mm inner diameter, a 25 mm outer diameter, a 20 mm diffusion path length, an adhesion environment containing a Whatman 40 cellulose filter (8 μm)/GFA (1.6 μm) filter and 200 μL an adsorbent with a composition of 74% glycerol (Merck), 15% Na_2CO_3 (Merck), and 11% NaNO_2 (Merck). Fig. 1(b) shows the schematic views and images of the passive samplers prepared in the laboratory.

2.1.1. Water absorption capacity measurement

A composite membrane can have a branched structure due to containing various types of hydrogen bonds and groups bound to the hydrogen bonds. The cross-linking agent consumes amine groups

in the branched structure and increases the hydrophilic degree of the membrane by breaking intermolecular and intramolecular hydrogen bonds [35]. The hydrophilic or hydrophobic degree of the composite membrane was evaluated by determining water absorption percentage, which is also related to the porosity of the membrane. First, the dry mass of the cross-section of 5x5 cm membrane was weighed, and then the cross-section of the membrane was kept in ultra-pure water at RT for 24 h. Finally, its mass was weighed again after the excess water was removed by a blotting paper. Water absorption percentage was calculated using these two values through the following equation below [36].

$$\text{Water absorption (\%)} = \frac{W_2 - W_1}{W_2} \times 100 \quad (2)$$

Where, W_1 shows the weight of dry membrane and W_2 shows the weight of membrane soaked in water for 24 h, at RT.

2.1.2. Determination of sampling rate

The ozone concentration in the air was calculated using Fick's First Law for badge- and tube-type samplers.

$$C_{\text{ozone}} = \left(\frac{m_a - m_b}{u_i \cdot t}\right) \quad (3)$$

where m_b shows the mass of the ozone (μg) found on the sorbent, m_a shows the mass of the ozone (μg) on a non-exposed sorbent (a blank), t (min) shows the sampling time, C shows the ambient concentration ($\mu\text{g}/\text{m}^3$) of the ozone, and U_i shows the uptake rate of the ozone (m^3/min). A "v" value (conversion factor from ozone to PA) of 0.448 in the Fick's First Law was used for the tube-type sampler.

Uptake rate is calculated through the diffusion coefficient and the geometry of the tube as follows:

$$U_i = D_i \cdot x \left(\frac{A}{L}\right) \quad (4)$$

where D_i shows the diffusion coefficient of the ozone in air (cm^2/min), A shows the area of the sampler (cm^2), and L shows the length of the diffusion zone (cm).

2.2. Sampler Analysis

The ozone collected in the adhesion environment for badge-type samplers was analyzed as NO_3^- a wavelength of 410 nm by a spectrophotometer, based on the EPA 352.1 method, after extracting it with 18 MW distilled water. Nitrate ion concentration was determined based on the reference calibration graph obtained using standard sodium nitrate (Merck) at a range from 1 to 10 $\mu\text{g}/\text{mL}$.

After sampling the tube-type samplers, the silica gel inside the tubes was extracted with 4.5 mL of 0.023 M MBTH (3-methyl-2-benzothiazolinone hydrazine, Fluka) solution, and the absorbance of the extracted solution was measured by a spectrophotometer at a wavelength of 430 nm [7]. The ozone concentration was determined based on the reference calibration graph obtained using standard ozone gas at a range from 2.67 to 14.22 $\mu\text{g}/\text{mL}$. PA (pyridine-4-aldehyde) concentration of the hydrolysis product was measured by a spectrophotometer at a wavelength of 430 nm.

3. Results and Discussion

3.1. Membrane Characterization

In this study, a gel-like membrane was produced first, and then a porous structure, shown in Fig. 2(a), was formed after extracting the membrane by hot water. The surface morphology of the membrane was obtained by SEM, as shown in Fig. 2(b).

Fig. 2(b) shows that there were very small pores on the surface of the composite membrane. This phenomenon may have occurred because brown sugar was used as a cross-linking agent to increase the flexibility and tensile strength of the membrane. The amount of cross-linking agent in the membrane significantly affects the porous structure. In a study conducted by [26], when the amount of cross-linking agent was 0.3%, the porosity was 62%, and when the concentration was increased to 2%, the porosity decreased to 25%. In the present study, the masses of the composite membrane before and after extraction were 1.254 and 0.445 g, respectively; the thickness of the membrane was 1 mm, and the porosity calculated using the Eq. (1) was 65%. The dry mass of the membrane was 0.442 g, while its mass was 0.621 g after keeping it in ultra-pure

water for 24 h. Water absorption of the composite membrane calculated using the Eq. (2) was 28%. Water absorption percentage is important for designing air samplers. A higher level of pollutant gas can be adsorbed and shorter sampling times can be achieved through the absorption of moisture from the air by the composite membrane.

Water vapor is absorbed by polar sorbents; their breakthrough capacity for the analyte is thereby reduced for most compounds. Collecting media may also be affected by humidity. Moisture may affect a media's collection efficiency. Gas molecules with low mass move faster than those with large mass. The mass of humid air is higher than that of the same volume of non-humid air. Consequently, the speed of the gas molecules increases with humidity absorbed in the diffusion barrier thus the gas is diffused faster from the static area to the collecting media. In such a case, a greater quantity of analyte is collected during a shorter sampling period [37, 38].

More pollutant gas adsorptions by adsorbent and shorter sampling times can be achieved through the absorption of moisture from the air by the composite membrane. Moreover, this feature was incorporated to the membrane not using toxic or mutagenic chemicals but using brown sugar, a biological cross-linker.

3.2. Validation of Passive Sampler

In 8-h and 15-d sampling periods, the standard deviation of 20 blank samples placed in the semi-urban and urban area was calculated and the detection limit was determined as three times the standard deviation. The 15-d average blank value was found to be $0.58 \pm 0.15 \mu\text{g}$ by placing 20 closed badge-type samplers at five different points protecting them from sun light. The 8-h average blank value was found to be $0.14 \pm 0.22 \mu\text{g}$ by placing 20 closed (at the head) tube-type samplers at five different points protecting them from sun light.

The repeatability of the badge and tube type samplers used in the study was determined by the relative standard deviation (RSD) of the blank results in the first step, and the area sampling results in the following step, which was calculated according to the following equation:

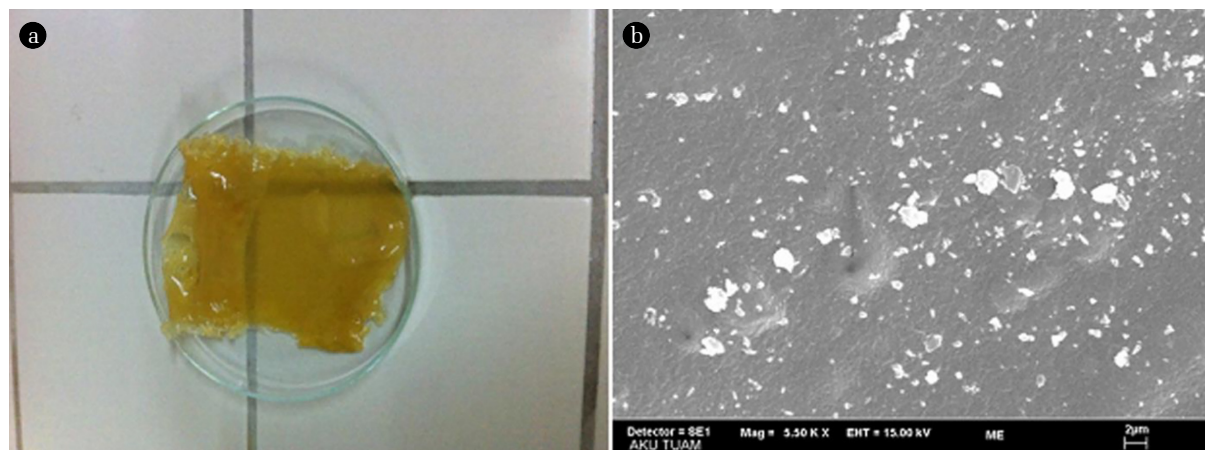


Fig. 2. (a) Laboratory image of composite membrane, (b) SEM micrograph of composite membrane.

$$RSD(\%) = \frac{S \times 100}{\bar{x}} \quad (5)$$

Where, s shows the standard deviation of sampling results of the same point and shows arithmetic mean of sampler results.

RSD < 10 was determined for 20 tube type blank samplers in the 8-h sampling period while RSD < 20 was determined for both tube and badge type blank samplers in the 15-day sampling period. RSD values were determined to be between 15% and 25% in eight different regions where five samplers were placed in each region.

The theoretical sampling rate of the classic tube-type sampler was calculated to be 4.691 cm³/min, setting A at 1.767 cm² and L at 6 cm constant, while that of the badge-type sampler was calculated to be 17.502 cm³/min, setting A at 3.461 cm², L at 2.1 cm, and molecular diffusion rate coefficient at 0.177 cm²/s (at 25°C and 1 atm). To determine the experimental sampling rate, 2 sets of samplings with 10 samplers, were conducted in a region where online ozone measurement was performed in a period having an average temperature of 14°C, a relative humidity of 35%, and a wind velocity of > 1m/s. Online ozone measurement results were taken for reference, and U_i (experimental sampling rate) calculated using C_{ozone} , the amount of ozone collected in the collecting media (ma) and the amount of ozone collected in the blank (mb); the values in equation (3) are shown in Table 2 below.

Average experimental sampling rates were found to be 55 cm³/min and 22.47 cm³/min for the tube-type and badge-type samplers, respectively. As shown in the table1, the developed passive sampler had a higher sampling rate than the current samplers and yielded equivalent results to those of automatic analyzer (Fig. 3).

A Gradko sampler is a Palmes type sampler which does not use a membrane as the diffusion barrier. Aerosol particles that contain high levels of nitrate lead to interference. Gradko tube type sampler is considered to have irreversible uptake of ozone on collecting medium. However, in this study, ozone diffused into the DPE by passing through the porous membrane by means of a different method. This method enabled the prevention possible attempts by blocking the entry of aerosols into the sampler that could react with DPE or ozone. Moreover, it was considered that the porous membrane prevented the escape of the ozone retained in the collecting medium to outdoor air, and thus, more ozone was retained in the collecting medium. In the Radiello sampler, PE membrane is used as the diffusion barrier. The developed membrane is hydrophilic, whereas the PE membrane is hydrophobic.

The relationship between the results of a passive sampler reinforced with composite membrane and automated O₃ monitors results was investigated at a station belonging to the Air Quality

Monitoring Network in Ankara, Turkey. The sampling rates of developed passive samplers were determined by correlating the amounts of ozone collected in the passive sampler (between March 21 and April 4, 2016) with the UV-photometric analyzer concentration values in Ankara/Turkey. The concentration values, obtained using the automatic analyzer were provided by the National Air Quality Monitoring Network coordinated by Turkish Ministry of Environment and Urbanization. Automatic analyzers are regularly calibrated every three months with portable O₃ generators certified with NIST UV long path photometer standards. Passive samplers were located in the shelter at a minimum distance of 3 cm between them and as close to the height of the sampling nozzle of automatic analyzers as possible. Passive samplers (5 blanks and 5 samplers) were subjected to the ambient air at the sampling point for 8 h (09.00-17.00) on and 13 successive days. Fig. 3 shows actual environment sampling results; these are in agreement with the results obtained by the UV-photometric measurement method, which was accepted as the reference method.

When the correlation of the results obtained for two different samplings was evaluated by regression analysis, the concordance ($R^2 = 0.855$) between two methods was good enough, as shown in Fig. 3. Researchers have generally preferred to use active samplers or automatic analyzers to evaluate passive samplers. In these studies, the relationship between active and passive sampling results was

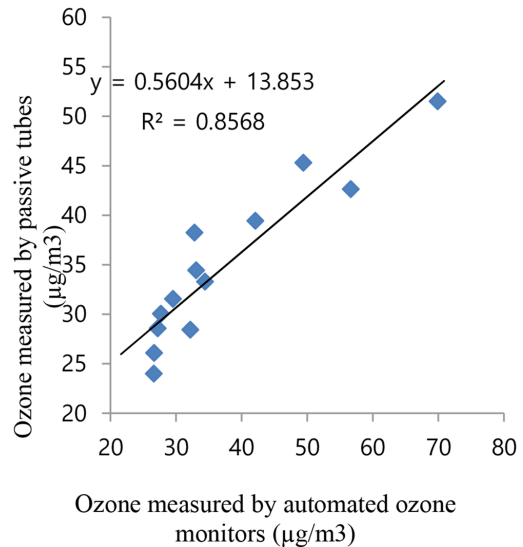


Fig. 3. The relationship between atmospheric concentrations of ozone measured by ozone monitors and by passive tubes using membrane as turbulence limiting diffuser (Ankara-Turkey).

Table 2. Experimental Sampling Rates Calculated For the Passive Sampler

Ozone measured by automated ozone monitors (µg/m ³)	Average Blank Value (µg) (n = 5)	Ozone measured by Passive Sampling (µg) (n = 5)	Average Experimental Sampling Rate (m ³ /h)
The tube-type samplers			
27.68 (8 h)	0.29 ± 0.06	1.08 ± 0.12	0.592E-04 ± 0.102E-04
29.52 (8 h)	0.34 ± 0.15	1.08 ± 0.30	0.527E-04 ± 0.107E-04
The badge-type samplers			
36.97 (2 week)	0.38 ± 0.12	0.78 ± 0.11	0.224E-04 ± 0.126E-04

determined in the range of ($R^2 = 0.67-0.88$) because environmental conditions such as temperature, wind velocity and pressure had a stronger effect on passive sampling performed in outdoor air [9, 39, 40]. At levels below $30 \mu\text{g}/\text{m}^3$, the measurements obtained with an automated ozone monitor were similar to those obtained with a passive sampler; however, it was also seen in this study that automated ozone monitor exhibited higher results at higher concentrations. As the automated ozone monitor method was accepted as the reference method, there is no doubt that its results are accurate. This method yields results in short periods such as an h; this is not sufficient time for substances that will cause positive or negative interference in the air and consume ozone. However, 8-h passive sampling, which is 8 times longer than that for active sampling is adequate for reactive species such as ozone to react and be consumed. Therefore, maintaining a high correlation between passive and active sampling of reactive species, including formaldehyde and ozone, is very difficult in ambient air. The relationship between passive and active sampling was higher in this study than in other studies. According to the F test results, there was no difference at a 99% significance level between the results of automatic analyzer and passive sampling ($p < 0.01$).

The % accuracy values of the developed passive samplers were calculated according to the following equation.

$$\text{Accuracy (\%)} = \frac{X_{\text{ref}} - X}{X_{\text{ref}}} \times 100 \quad (6)$$

Where X_{ref} shows atmospheric concentration of ozone measured by reference method and X shows atmospheric concentration of ozone measured by passive tubes using membrane as turbulence limiting diffuser.

UV-photometric analyzer results were used as reference method values in determining the accuracy values. The mean accuracy of tube type passive samplers was determined as 6.82%.

The storage stability of the developed passive sampler was investigated in two stages as pre-sampling (shelf life) and post-sampling

(storage). Five ready-to-use tube type passive samplers were stored in the refrigerator at $+4^\circ\text{C}$ for 3 months and these newly prepared samplers and the old samples were left to 8 h sampling in semi-rural area. The results were compared and the difference between the old and new samplers was found to be quite small ($\text{RSD} < 10$) and appropriate according to CEN protocol. The storage stability of the passive samplers was determined by exposing five passive samplers to an ozone concentration of $52.01 \mu\text{g}/\text{m}^3$ and then leaving them in a refrigerator at 4°C for three months. The analyses showed that the passive samplers developed and produced in the present study remained robust for three months, from sampling to analysis, under laboratory conditions at 4°C .

O_3 recoveries was performed by spiking the standard ozone gas in the sampler and the lowest recovery was 85% for $2.67 \mu\text{g}/\text{mL}$ ozone concentration

3.2.1. Evaluation of passive samplers under field conditions

Passive samplers reinforced with a composite membrane were tested in land conditions at the Selçuk University Campus in Konya, which is accepted to be a semi-urban area. The passive samplers were subjected to ambient air to test their ozone absorption performance. Samplers were placed in dark-colored plastic shelters at 100 cm above the earth to protect them from environmental conditions such as rain and sun light. Badge and tube-type samplers were placed in the same shelters and subjected to two different sampling times: 8 h and 15 d. The results are shown in Table 3.

Table 3 indicates that although the sampling rates of badge-type samplers were higher than those of tube-type samplers [41], parallel sampling results showed that higher concentration values were obtained with tube-type samplers reinforced with the composite membrane. The experimental sampling rate was found to be higher in the tube-type sampler reinforced with the composite membrane than in the badge-type sampler. This result was also supported by the sampling results. Area sampling results revealed that the current badge-type sampler was not suitable for 8-h area samplings, but that tube-type samplers could be used for that purpose. Because

Table 3. Comparison of Atmospheric O_3 Concentrations from Different Samplers

Exposure time	Badge-type sampler		Tube-type sampler	
	Summer Period	Winter Period	Summer Period	Winter Period
8-h-sampling (09.00-17.00)	Not determined	Not determined	81.53 ± 0.29	21.46 ± 0.28
15 d	38.45 ± 0.49	10.78 ± 0.33	52.01 ± 0.52	16.52 ± 0.32

Table 4. Concentrations of O_3 in Konya's Atmosphere as Determined by Tube-type Passive Sampling ($\mu\text{g}/\text{m}^3$)

Site type/location	Mean Conc. \pm S.D. (n = 5)	Min	Max.
Urban/Selçuklu	79.05 ± 0.27	78.16	80.55
Sub-Urban/Selçuklu	88.40 ± 0.33	88.15	91.19
Industrial-1/Selçuklu	92.49 ± 0.30	87.99	93.58
Industrial-2/Selçuklu	81.77 ± 0.26	81.22	82.28
Sub-Urban/Selçuklu	82.75 ± 0.28	82.05	83.81
Urban/Selçuklu	81.57 ± 0.21	81.48	81.67
Urban/Karatay	69.48 ± 0.29	66.44	69.80
Urban/Meram	87.48 ± 0.29	86.59	88.56

the O₃ parameter could not be continuously measured by the online measurement method in the ambient air of Konya, 8-h ozone measurements (09.00-17.00) were performed by the passive sampler reinforced with the composite membrane at different locations in May. The results are shown in Table 4.

When O₃ monitoring results obtained from different regions of Konya were evaluated, the highest values were observed at the sampling point (Industrial-1/Selçuklu) near the organized industrial zone in Selçuklu County, while the lowest O₃ levels were found at the sampling point of Urban/Karatay, as indicated in Table 4. Similar results were obtained at the other sampling points. In a study using Gradko passive diffusion tubes to determine O₃ levels in Konya in 2010, 15-day mean concentrations in the summer period were found to range from 54 to 98 µg/m³ [42]. In a study conducted by [43] using passive samplers at 60 points in İskenderun, Turkey, O₃ levels were determined to range from 11 to 395 µg/m³. A study conducted by [44] using passive samplers at 49 points in Aliğa/İzmir, Turkey found that O₃ concentrations ranged from 24 to 134 µg/m³. The results found in the present study were similar to the high ozone concentration levels determined in industrial and rural areas in the above-mentioned studies.

4. Conclusions

In this study, promising results were obtained for sampling ozone with a composite membrane reinforced passive sampler in ambient air. A composite membrane was used as a diffuser in the developed passive sampler, and higher sampling rates were obtained than the classical passive samplers. The results for 8-h sampling time were equivalent to those obtained by automated ozone monitoring. The composite membrane did not change the sampling rate even in different wind velocities by preventing the eddy diffusion resulting from the diffuser's air turbulence, which considered being the most important factor in obtaining equivalent results from online measurements with passive samplers. The developed passive sampler can be used even in winter-area samplings that include low ozone concentrations. Moreover, it is easy and practical to use and therefore does not require any specialty on its use. This study demonstrated that the developed passive sampler can be used to determine the O₃ emissions at high concentration levels in summer period. The passive samplers with high repeatability (RSD < 10) and low blank values are suitable for use indoors as well as for field sampling.

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Author Contributions

G.K. (Asst. Prof. Dr.) designed and conducted all the experiments and wrote the manuscript.

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